



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



⑪ Publication number: 0 542 374 A1

⑫

## EUROPEAN PATENT APPLICATION

⑬ Application number: 92203471.5

⑮ Int. Cl. 5: C08G 12/30

⑭ Date of filing: 12.11.92

Amended claims in accordance with Rule 86 (2)  
EPC.

⑯ Priority: 14.11.91 IT MI913044

⑰ Date of publication of application:  
19.05.93 Bulletin 93/20

⑱ Designated Contracting States:  
AT BE CH DE DK ES FR GB IT LI NL SE

⑲ Applicant: MINISTERO DELL' UNIVERSITA' E  
DELLA RICERCA SCIENTIFICA E  
TECNOLOGICA  
76, Lungotevere Thaon di Revel  
I-00196 Roma (IT)

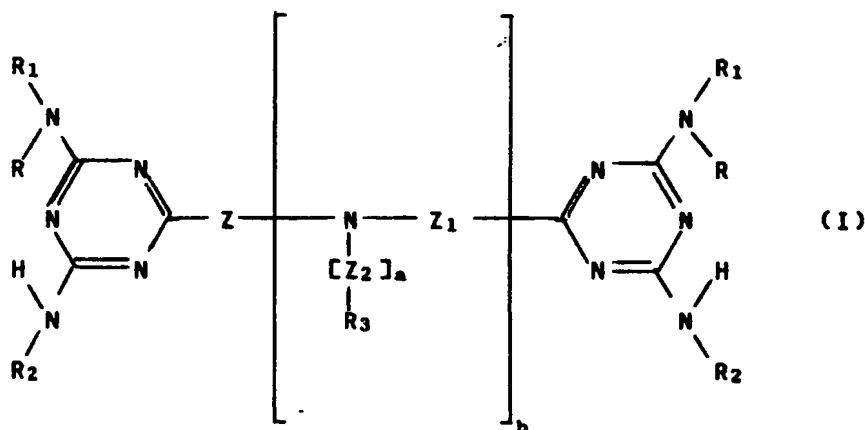
⑳ Inventor: Cipolli, Roberto

Viale A. Volta, 33  
I-28100 Novara (IT)  
Inventor: Oriani, Roberto  
Via Monte Ortigara, 22  
I-20137 Milan (IT)  
Inventor: Maserati, Enrico  
Via Pianello, 321  
I-29010 Castelnovo Val Tidone  
(Piacenza) (IT)  
Inventor: Nuclida, Gilberto  
Via Mazzini 14  
I-20098 San Giuliano Milanese (Milan) (IT)

㉑ Representative: Roggero, Sergio et al  
Ing. Barzanò & Zanardo Milano S.p.A. Via  
Borgonuovo 10  
I-20121 Milano (IT)

㉒ Melaminic polycondensates.

㉓ Condensation compounds obtained by means of the polymerization of polyaminic compositions essentially constituted by derivatives of 2,4,6-triamino-1,3,5-triazine, having the general formula (I):



with aldehydes, preferably formaldehyde.

EP 0 542 374 A1

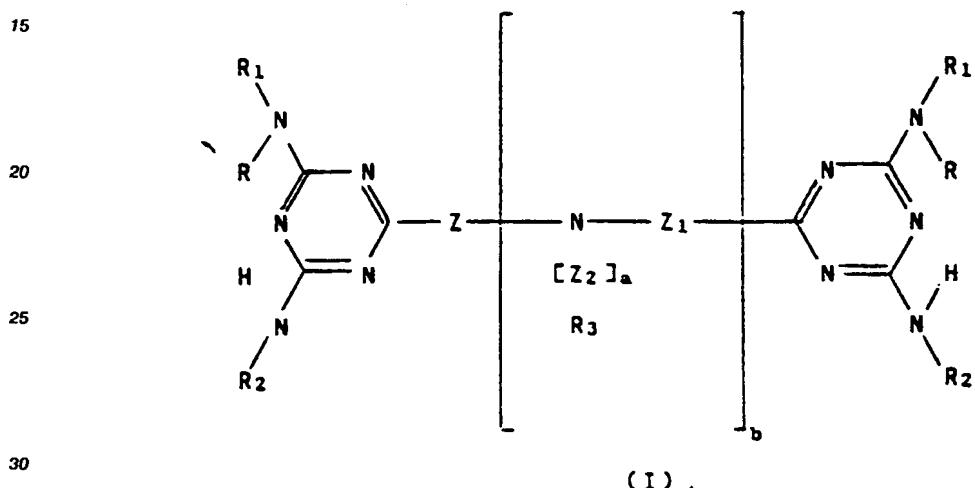
The present invention relates to compounds obtained by means of polycondensation of polyaminic compositions, essentially constituted by melaminic derivatives, with aldehydes.

More particularly, the present invention relates to compounds of polycondensation with aldehydes, preferably formaldehyde, of derivatives of 2,4,6-triamino-1,3,5-triazine.

These compounds are used in the preparation of self-extinguishing polymeric compositions, based on thermoplastic polymers, or polymers endowed with elastomeric properties, in particular olefinic polymers or copolymers, in combination with ammonium or amine phosphates and/or phosphonates.

In particular, the subject matter of the present invention are the aminoplastic resins obtained by means of the polymerization of a mixture comprising:

(1) from 0 to 50 parts by weight of one or more polyaminic derivatives;  
 (2) from 50 to 100 parts by weight of one or more derivatives of 2,4,6-triamino-1,3,5-triazine having the general formula (I):



with formaldehyde or a mixture of formaldehyde and an aldehyde having the general formula (II):

35 R<sub>4</sub> - CHO (II)

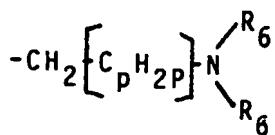
wherein the aldehyde having the general formula (II) can be present in an amount of up to 20% by mol, and wherein:

40 the radicals from R to R<sub>2</sub>, which may be the same, or different from each other, and may have different meanings on each triazinic ring, are:

45 H; C<sub>1</sub> - C<sub>18</sub> alkyl; C<sub>2</sub> - C<sub>8</sub> alkenyl; C<sub>6</sub> - C<sub>16</sub> cycloalkyl or alkylcycloalkyl, possibly substituted with a hydroxy or C<sub>1</sub> - C<sub>4</sub> hydroxalkyl function;

-CH<sub>2</sub>{C<sub>m</sub>H<sub>2m</sub>}O - R<sub>6</sub>

45



wherein:

55 m = an integer comprised within the range of from 1 to 7;

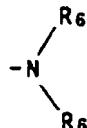
p = an integer comprised within the range of from 1 to 5;

R<sub>6</sub> = H; C<sub>1</sub> - C<sub>8</sub> alkyl; C<sub>2</sub> - C<sub>6</sub> alkenyl; {C<sub>q</sub>H<sub>2q</sub>}O - R<sub>7</sub> wherein q is an integer comprised within the range of from 1 to 4 and R<sub>7</sub> is H or C<sub>1</sub> - C<sub>4</sub> alkyl; C<sub>6</sub> - C<sub>12</sub> cycloalkyl or alkylcycloalkyl;

the radicals  $R_6$ , which may be the same, or different from each other, are:

$H$ ,  $C_1 - C_8$  alkyl;  $C_2 - C_6$  alkenyl;  $C_6 - C_{12}$  cycloalkyl or alkylcycloalkyl;  $C_1 - C_4$  hydroxyalkyl; or the moiety:

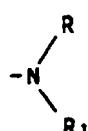
5



10

is replaced by a heterocyclic radical linked to the alkyl chain through the nitrogen atom, and possibly containing another heteroatom preferably selected from  $O$ ,  $S$ ,  $N$ ; or in the general formula (I) the moiety:

15



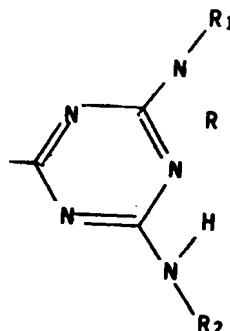
20

is replaced by a heterocyclic radical linked to the triazinic ring through the nitrogen atom, and possibly containing another heteroatom preferably selected from  $O$ ,  $S$ ,  $N$ ;

25

- a is 0 (zero) or 1;
- b is 0 (zero) or an integer comprised within the range of from 1 to 5;
- $R_3$  is hydrogen or:

30



35

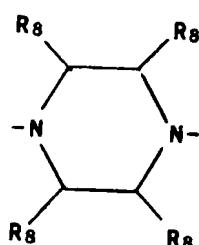
40

and its meaning may vary within each repeating unit; when b is 0 (zero),  $Z$  is a divalent radical falling within the scope of one of the following formulas:

45

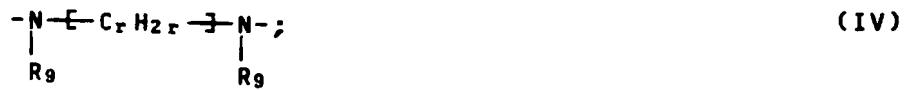
50

(III)

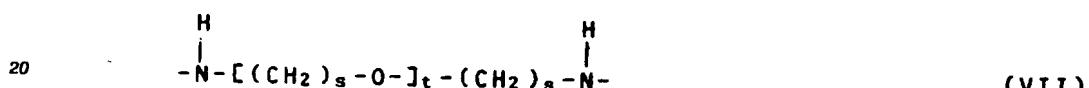
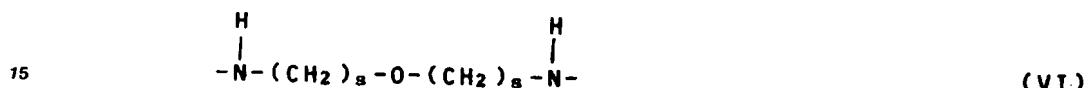


55

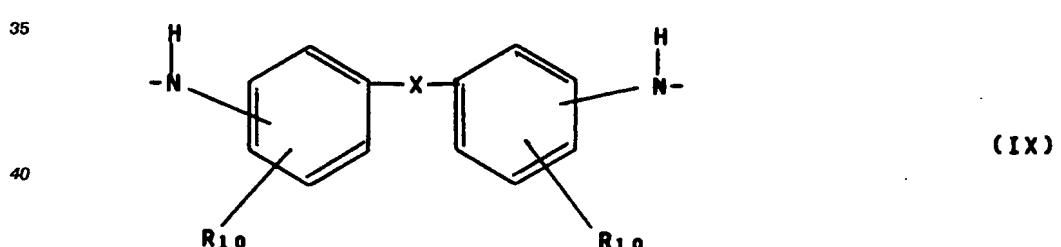
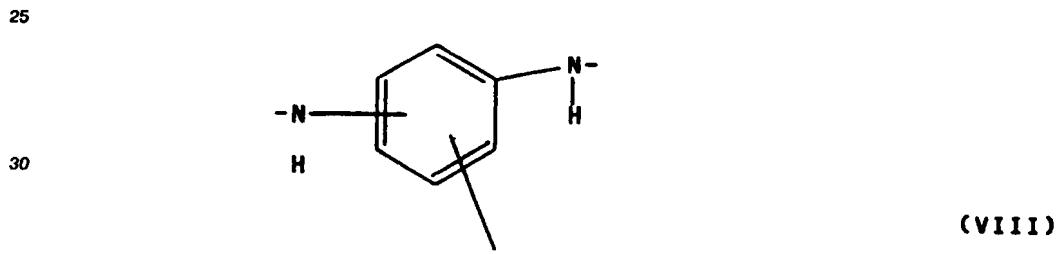
wherein the radicals  $R_8$ , which may be the same or different from each other, are hydrogen or  $C_1 - C_4$  alkyl;



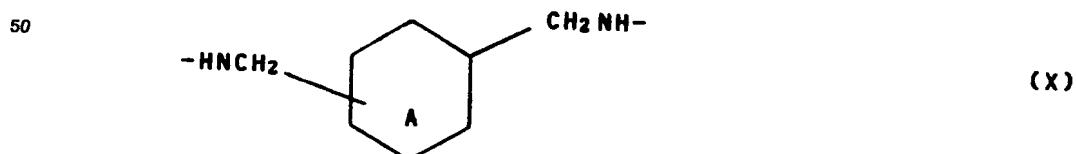
10 wherein r is an integer comprised within the range of from 2 to 14; R<sub>9</sub> is hydrogen; C<sub>1</sub> – C<sub>4</sub> alkyl; C<sub>2</sub> – C<sub>6</sub> alkenyl; C<sub>1</sub> – C<sub>4</sub> hydroxyalkyl;



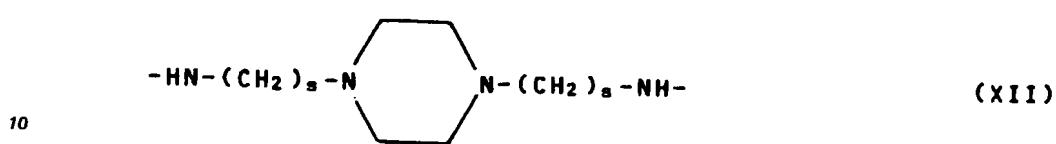
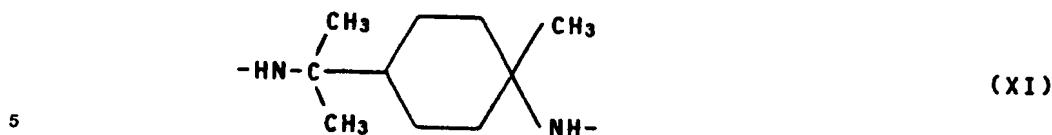
wherein s is an integer comprised within the range of from 2 to 5 and t is an integer comprised within the range of from 1 to 3;



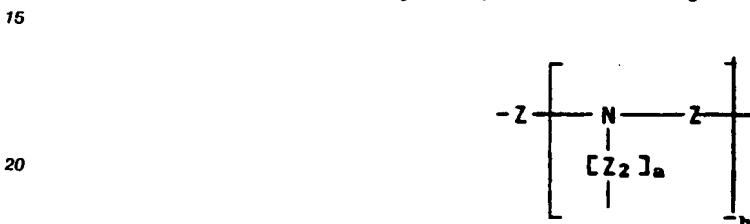
45 wherein:  
X is a direct C – C bond; O; S; S – S; SO; SO<sub>2</sub>; NH; NHSO<sub>2</sub>; NHCO; N = N; CH<sub>2</sub>;  
 $R_{10}$  is hydrogen; hydroxy; C<sub>1</sub> – C<sub>4</sub> alkyl; C<sub>1</sub> – C<sub>4</sub> alkoxy;



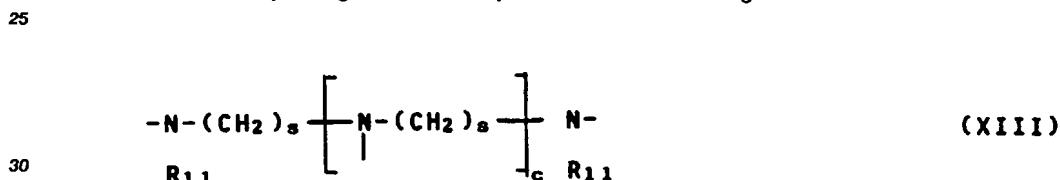
wherein A may be a saturated or unsaturated ring:



wherein s has the above defined meaning;  
when, on the contrary, b is an integer comprised within the range of from 1 to 5, the moiety:

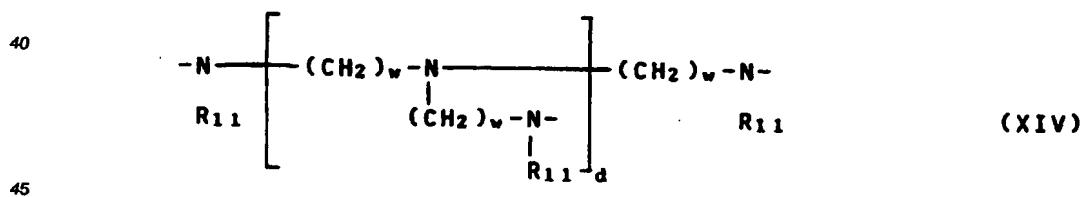


is a multivalent moiety falling within the scope of one of the following formulas:



wherein:

35  $R_{11}$  is hydrogen or  $C_1 - C_4$  alkyl;  
 $c$  is an integer comprised within the range of from 1 to 5;  
the indexes s, which may be the same, or different from each other, have the same meaning as defined hereinabove;



wherein:

50  $R_{11}$  has the meaning as defined hereinabove;  
 $w$  is an integer comprised within the range of from 2 to 4;  
 $d$  is either 1 or 2.  
 $R_4$  is  $C_1 - C_8$  alkyl;  $C_2 - C_6$  alkenyl;  $C_6 - C_{12}$  cycloalkyl;  $C_6 - C_{12}$  aryl, possibly substituted with one or more  $C_1 - C_4$  alkyl radicals;  $C_7 - C_{16}$  aralkyl;  $C_8 - C_{12}$  aralkenyl.

According to a preferred form of practical embodiment of the aminoplastics according to the present invention, the polyaminic derivative is selected from compounds containing the 1,3,5-triazine ring, or at least one  $>C=O$  and/or  $>C=S$  moiety.

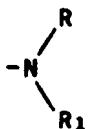
Also those derivatives having an asymmetrical structure, in the sense that the radicals  $R$ ,  $R_1$  and  $R_2$  may have different meanings on each triazinic ring, fall within the scope of general formula (I).

Examples of radicals from R to R<sub>3</sub> in general formula (I) are:

methyl; ethyl; propyl; isopropyl; n – butyl; isobutyl; tert – butyl; n – pentyl; isopentyl; n – hexyl; tert – hexyl; octyl; tert – octyl; decyl; dodecyl; octadecyl; ethenyl; propenyl; butenyl; isobut enyl; hexenyl; octenyl; cyclohexyl; propylcyclohexyl; butylcyclohexyl; decylcyclohexyl; hydroxycyclohexyl; hydroxyethylcyclohexyl;

5 2 – hydroxyethyl; 2 – hydroxypropyl; 3 – hydroxypropyl; 3 – hydroxybutyl; 4 – hydroxybutyl; 3 – hydroxy pentyl; 5 – hydroxypentyl; 6 – hydroxyhexyl; 3 – hydroxy – 2,5 – dimethylhexyl; 7 – hydroxyheptyl; 7 – hydroxyoctyl; 2 – methoxyethyl; 2 – methoxypropyl; 3 – methoxypropyl; 4 – methoxybutyl; 6 – methoxyhexyl; 7 – methoxyheptyl; 7 – methoxyoctyl; 2 – ethoxyethyl; 3 – ethoxypropyl; 4 – ethoxybutyl; 3 – propoxypropyl; 3 – butoxypropyl; 4 – butoxybutyl; 4 – isobutoxybutyl; 5 – propoxypentyl; 2 – cyclohexyloxyethyl; 2 – ethenylloxethyl; 10 2 – (N,N – dimethylamino) ethyl; 3 – (N,N – dimethylamino) propyl; 4 – (N,N – dimethylamino) butyl; 5 – (N,N – dimethylamino) pentyl; 4 – (N,N – diethylamino) butyl; 5 – (N,N – diethylamino) pentyl; 5 – (N,N – diisopropylamino) pentyl; 3 – (N – ethylamino) propyl; 4 – (N – methylamino) butyl; 4 – (N,N – dipropylamino) butyl; 2 – (N,N – diisopropylamino) ethyl; 6 – (N – hexenylamino) hexyl; 2 – (N – ethenylamino) ethyl; 2 – (N – cyclohexylamino) ethyl; 2 – (N – 2 – hydroxyethylamino) ethyl; 2 – (2 – hydroxyethoxy) ethyl; 2 – (2 – methoxyethoxy) ethyl; 6 – (N – propylamino) hexyl; and so forth.

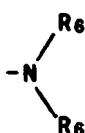
Examples of heterocyclic radicals which may replace the moiety:



25 in general formula (I) are:

aziridine; pyrrolidine; piperidine; morpholine; thiomorpholine; piperazine; 4 – methylpiperazine; 4 – ethyl – piperazine; 2 – methylpiperazine; 2,5 – dimethylpiperazine; 2,3,5,6 – tetramethylpiperazine; 2,2,5,5 – tetramethylpiperazine; 2 – ethylpiperazine; 2,5 – diethylpiperazine; and so forth.

Examples of heterocyclic radicals which may replace the moiety:



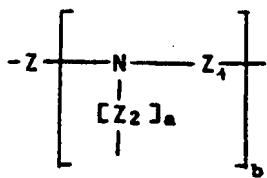
35

are:

aziridine; pyrrolidine; piperidine; morpholine; thiomorpholine; piperazine; 4 – methylpiperazine; 4 – ethyl – piperazine; and so forth.

40 Examples of divalent – Z – radicals are those which derive, by elimination of a hydrogen atom from each aminic moiety, from the following diaminic compounds: piperazine; 2 – methyl piperazine; 2,5 – dimethylpiperazine; 2,3,5,6 – tetramethyl piperazine; 2 – ethylpiperazine; 2,5 – diethyl piperazine; 1,2 – diaminoethane; 1,3 – diaminopropane; 1,4 – diaminobutane; 1,5 – diaminopentane; 1,6 – diaminohexane; 1,8 – diaminooctane; 1,10 – diaminodecane; 1,12 – diaminododecane; N,N – dimethyl – 1,2 – diaminoethane; N – methyl – 1,3 – diaminopropane; N – ethyl – 1,2 – diaminoethane; N – isopropyl – 1,2 – diaminoethane; N – (2 – hydroxyethyl) – 1,2 – diaminoethane; N,N' – bis (2 – hydroxyethyl) – 1,2 – diaminoethane; N – (2 – hydroxyethyl) – 1,3 – diaminopropane; N – hexenyl – 1,6 – diaminohexane; N,N' – diethyl – 1,4 – diamino – 2 – butene; 2,5 – diamino – 3 – hexene; 2 – aminoethyl ether; (2 – aminoethoxy) methylether; 1,2 – bis – (2 – aminoethoxy) ethane; 1,3 – diaminobenzene; 1,4 – diaminobenzene; 2,4 – diaminotoluene; 2,4 – dia minoanisole; 2,4 – diaminophenol; 4 – aminophenylether; 4,4' – methylenedianiline; 4,4' – diaminobenzanilide; 3 – aminophenylsulfone; 4 – aminophenylsulfone; 4 – aminophenylsulfoxide; 4 – aminophenyldisulfide; 1,3 – bis (aminomethyl) benzene; 1,4 – bis (aminomethyl) benzene; 1,3 – bis (aminomethyl)cyclohexane; 1,8 – diamino – p – mentane; 1,4 – bis (2 – aminoethyl) piperazine; 1,4 – bis (3 – aminopropyl) piperazine; 1,4 – bis (4 – aminobutyl) piperazine; 1,4 – bis (5 – aminopentyl) piperazine; and so forth.

55 Examples of multivalent radicals:



are those which derive, by elimination of a hydrogen atom from each reacted amino group, from the  
10 following polyaminic compounds:

bis (2 - aminoethyl) amine; bis (3 - aminopropyl) - amine; bis (4 - aminobutyl) amine; bis (5 - aminopentyl) -  
amine; bis [2 - (N - methylamino) ethyl] amine; 2 - N - butyl - bis (2 - aminoethyl) amine; bis [3 - (N -  
methylamino) - propyl] amine; N - (3 - aminopropyl) - 1,4 - diamonobutane; N - (3 - aminopropyl) - 1,5 -  
15 diaminopentane; N - (4 - aminobutyl) - 1,5 - diaminopentane; tris (2 - aminoethyl) amine; tris (3 -  
aminopropyl) amine; tris (4 - aminobutyl) amine; tris [2 - (N - ethylamino) ethyl] amine; N,N' - bis (2 -  
aminoethyl) - 1,2 - diaminoethane; N,N' - bis (3 - aminopropyl) - 1,3 - diaminopropane; N,N' - bis (2 -  
aminoethyl) - 1,3 - diaminopropane; N,N' - bis (3 - aminopropyl) - 1,2 - diaminoethane; N,N' - bis (3 -  
aminopropyl) - 1,4 - diaminobutane; bis [2 - (2 - aminoethyl) aminoethyl] amine; N,N' - bis [2 - (2 -  
aminoethyl) aminoethyl] - 1,2 - diaminoethane; N,N' - bis [3 - (2 - aminoethyl) aminopropyl] - 1,2 - dia -  
20 minoethane; N,N,N',N' - tetrakis (2 - aminoethyl) - 1,2 - diaminoethane; and so forth.

By "formaldehyde", as this term is used in the instant disclosure and in the appended claims, any forms are meant, in which formaldehyde is usually marketed: aqueous solution, metaformaldehyde, paraformaldehyde.

Examples of R<sub>4</sub> radical in general formula (II) are:

25 methyl; ethyl; n - propyl; isopropyl; n - butyl; isobutyl; tert - butyl; n - pentyl; isopentyl; n - hexyl; n - heptyl;  
isoheptyl; n - octyl; ethenyl; propenyl; isobutenyl; sec - butenyl; n - pentenyl; cyclohexyl; phenyl; 2 -  
methylphenyl; 3 - methylphenyl; 4 - methylphenyl; 4 - isopropylphenyl; 2,4,6 - trimethylphenyl; 1 -  
phenylethyl; 2 - phenylethyl; 2 - phenylethenyl; and so forth.

Examples of polyaminic derivatives are:

30 urea; ethyleneurea; propyleneurea; thiourea; ethylenethiourea; melamine; acetoguanamine; pro -  
pionoguanamine; butyroguanamine; isobutyroguanamine; caprinooguanamine; succinoguanamine; ben -  
zoguanamine; metamethylbenzoguanamine; benzylguanamine; hydantoin; piperazine - 2,5 - dione; barbituric  
acid; and so forth.

The aminoplastic resins according to the present invention can be synthetized as follows:

35 (a) by reacting in a suitable solvent (such as, e.g., water, methyl alcohol, ethyl alcohol, or their mixtures,  
and so forth), the derivative of 2,4,6 - triamino - 1,3,5 - triazine having the general formula (I), either  
mixed or not mixed with the polyaminic derivative, with formaldehyde or a mixture of formaldehyde and  
an aldehyde of general formula (II). The molar ratio of the derivative of general formula (I), or of its  
40 mixture with the polyaminic derivative, to formaldehyde, or to the mixture of formaldehyde with the  
aldehyde of general formula (II), is comprised within the range of from 1 : 1 to 1 : 12.

The reaction is carried out at a pH value comprised within the range of from 7 to 12, possibly obtained  
by adding an alkali (such as, for example, potassium carbonate, sodium carbonate, sodium hydroxide,  
and so forth), at temperatures comprised within the range of from 20 °C the boiling point of the solvent,  
until a finely subdivided dispersion is obtained;

45 (b) causing the resulting reaction product, constituted by the alkylol derivative, to turn into a resin by  
acidifying it to a pH value comprised within the range of from 1 to 5, by means of the addition of an acid  
(such as, e.g., sulfuric acid, hydrochloric acid, phosphoric acid, and so forth) and heating it to a  
temperature comprised within the range of from 40 °C to the boiling point of the solvent. The resulting  
50 dispersion is kept further stirred at the selected temperature, during the necessary time to complete the  
resinification process, preferably of from 1 to 12 hours. The residual acidity of the resulting mixture is  
then neutralized with a base selected from those as suggested hereinabove, and the resulting product is  
filtered off.

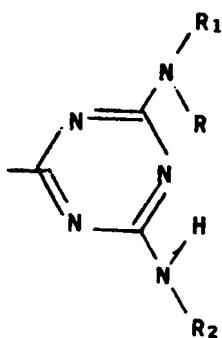
The resin is first dried at 100 °C, then is submitted to thermal treatment for some hours, preferably from  
1 to 3 hours, in a vacuum oven at 150 °C.

55 In general good quality aminoplastic resins are obtained as white crystal line powders, which are  
insoluble in water and can be used in self - extinguishing polymeric compositions without any further  
purification.

An alternative synthesis method consists in causing the reactions of the above (a) and (b) steps to take place in one single step, at a pH value comprised within the range of from 1 to 5, and at a higher temperature than 40 °C.

Many of derivatives of 2,4,6-triamino-1,3,5-triazine of general formula (I) are known; they can 5 anyway be easily synthetized according to as disclosed in European Patent application publication No. 415 371, to the same Applicant's name.

Condensation compounds obtained by means of the polymerization with aldehydes, preferably formaldehyde, of the melaminic derivatives of general formula (I), either containing, or not containing, polyaminic 10 derivatives, not cited in the Examples, are those as reported in Table 1, in which R<sub>3</sub>, when present, is substituted by the triazinic ring of formula:



5  
10  
15  
20  
25  
30  
35  
40  
45  
50

TABLE 1

COMPOUND N°	Derivative of general formula (I)		Polyaminic derivative	R <sub>4</sub> - CHO	R <sub>4</sub> mol x	Molar ratio polyamines / aldehydes
	R	N — R <sub>1</sub>				
1		H			—	1:4
2		H			—	1:3.5
3	H	H			—	1:2.5
4	(CH <sub>2</sub> ) <sub>2</sub> OCH <sub>3</sub>	(CH <sub>2</sub> ) <sub>2</sub> OCH <sub>3</sub>	H		—	—
5		H			C <sub>2</sub> H <sub>5</sub>	10
6	(CH <sub>2</sub> ) <sub>5</sub> OH	H	H		—	—
7	(CH <sub>2</sub> ) <sub>3</sub> OCH <sub>3</sub>	H	(CH <sub>2</sub> ) <sub>3</sub> OCH <sub>3</sub>		—	—
8		H			—	—

5  
10  
15  
20  
25  
30  
35  
40  
45  
50

TABLE 1 (continuation)

COMPOUND N°	Derivative of general formula (I)			Polyaminic derivative % designation by weight	R <sub>4</sub> - CHO	Molar ratio polyamines aldehydes
	R	R <sub>1</sub>	R <sub>2</sub>			
9	(CH <sub>2</sub> ) <sub>3</sub> N	H	H	-N	-Z <sub>1</sub> -	1:4
10	N	H	H	-HN(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH-	—	1:2.5
11	(CH <sub>2</sub> ) <sub>2</sub> OCH <sub>3</sub>	H	H	-HNC <sub>2</sub> H <sub>4</sub> -N-C <sub>2</sub> H <sub>4</sub> NH-	Aceto- guanamine	30
12	N	H	H	-HNCH <sub>2</sub> CH <sub>2</sub> NH-	—	1:6
13	N	H	H	-N	i-C <sub>6</sub> H <sub>9</sub>	8
14	CH <sub>2</sub> CH <sub>2</sub> OH	H	H	-HN- C(CH <sub>3</sub> ) <sub>2</sub> - C(CH <sub>3</sub> ) <sub>2</sub> - NH-	—	1:5
15	CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	H	H	-HN(CH <sub>2</sub> ) <sub>4</sub> NH-	Melamine	40
16	N	H	H	-HNCH <sub>2</sub> CH <sub>2</sub> NH-	—	1:8

TABLE 1 (continuation)

COMPOUND N°	Derivative of general formula (I)			Polyaminic derivative %	R <sub>4</sub> · CHO	R <sub>4</sub> · CHO	Molar ratio polyamines aldehydes
	R	N — R <sub>1</sub>	R <sub>2</sub>		R <sub>4</sub>	mol x	
17	H	H	H	N(CH <sub>2</sub> CH <sub>2</sub> NH) <sub>3</sub>	—	—	1:8
18	H	H	H		Benzyl- guanamine	35	—
19					—	—	1:3.5
20	H	H	H		Melamine	20	i-C <sub>3</sub> H <sub>7</sub> 8 1:3 1:2.5
21					·HNCH <sub>2</sub> CH <sub>2</sub> NH ·	—	— 1:4
22	H	H	H		·HNC <sub>2</sub> H <sub>4</sub> · N · C <sub>2</sub> H <sub>4</sub> NH ·	20	— 1:8
23					Piperazine- 2,5-dione	—	Succino- guanamine 18 1:4.5
24	<i>n</i> · C <sub>4</sub> H <sub>9</sub>	H	<i>n</i> · C <sub>4</sub> H <sub>9</sub>		—	—	— 1:4

The Examples disclosed in the following illustrate the features of the invention without limiting them.

55 Example 1

184.5 g of cyanuric chloride and 1300 cm<sup>3</sup> of methylene chloride are charged to a reactor of 3 litres of capacity, equipped with stirring means, thermometer, addition funnel, refluxing condenser and cooling bath.

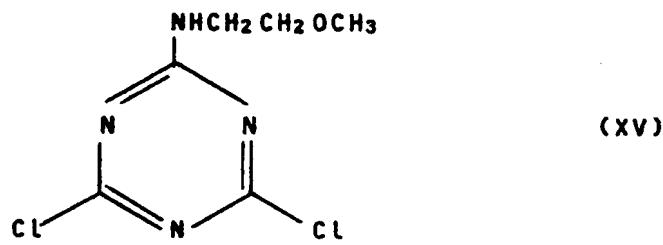
With cooling from the outside, 75 g of 2-methoxyethylamine and 40 g of sodium hydroxide dissolved in 150 cm<sup>3</sup> of water are added simultaneously, within a 3 hour time, with the pH value of the mixture being kept comprised within the range of from 5 to 7, and the temperature being kept comprised within the range of from 0 to 3°C.

5 The reaction mixture is kept at said temperature of 0–3°C for a further 3 hours, then the aqueous phase is separated.

The organic solution is treated with two portions of 200 cm<sup>3</sup> each, of water, with the aqueous phase being separated each time.

By distillation of methylene chloride, 217 g of intermediate (XV):

10



are obtained as a white crystalline powder with m.p. = 73–75°C (m.p. = melting point) and a chlorine content of 31.68% (theoretical chlorine content: 31.84%).

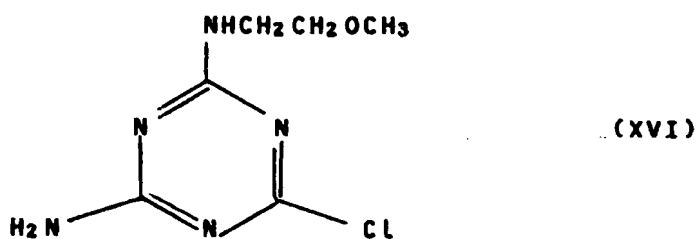
25 400 cm<sup>3</sup> of acetone and 133.8 g of intermediate (XV) are charged to a reactor of 1 litre of capacity equipped with stirring means, thermometer, addition funnel, refluxing condenser and heating bath.

The reaction mixture is heated up to 40°C with stirring, until a solution is obtained, then, with the temperature being kept constant at 40°C, 102 g of an aqueous solution of ammonia at 30% by weight are added during a 30 minute time.

30 The reaction mixture is subsequently heated up to 45°C, and is kept 4 hours at that temperature. After cooling down to 10°C, the resulting product is filtered off and is washed on the same filter with cold water.

After oven-drying at 100°C, 114 g of intermediate (XVI):

35



45 are obtained as a white crystalline powder having m.p. = 195–197°C, and a chlorine content of 17.18% (theoretical chlorine content: 17.44%).

500 cm<sup>3</sup> of xylene, 81.4 g of intermediate (XVI) and 17.2 g of piperazine are charged to the same reactor of 1 litre of capacity.

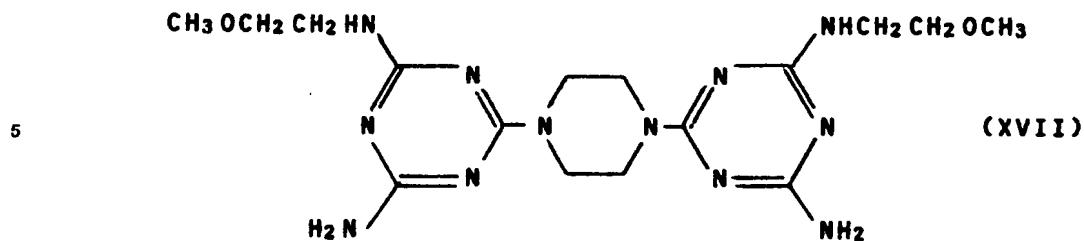
The resulting mixture is heated up to 100°C and is kept 2 hours at that temperature.

Then, 16 g of sodium hydroxide are added and the temperature of the reaction mixture is increased up 50 to boiling temperature. The reaction mixture is kept refluxing for approximately 20 hours, then is cooled down to room temperature, and the resulting precipitate is filtered off.

The filter cake is washed with a plentiful water and is dried.

74.2 g of intermediate (XVII):

55



10

with m.p. = 212–215°C are obtained.

The structure of intermediates (XV), (XVI) and (XVII) was confirmed by I.R. spectroscopic analysis.

450 cm<sup>3</sup> of water, 64.8 g of an aqueous solution at 37% by weight of formaldehyde, 0.7 g of sodium carbonate and, with stirring, 84.0 g of intermediate (XVII) are charged to the same reactor of one litre of capacity.

The reaction mass is heated up to 70°C, and is kept stirred at that temperature for five hours.

Then, 3.0 g of sulfuric acid diluted with 10 cm<sup>3</sup> of water are added.

The reaction mass is heated up to boiling temperature, and is kept under refluxing conditions for five hours.

20 Then, 200 cm<sup>3</sup> of water are added, with the temperature of the reaction mixture being allowed to decrease down to 60°C, and the reaction mixture is subsequently neutralized by means of the addition of 2.4 g of sodium carbonate.

The reaction mixture is kept at 60°C for one further hour, then the resulting product is filtered off, and the filter cake is washed on the same filter with hot water.

25 By oven drying the filter cake at 100°C and subsequently submitting it to a thermal treatment at 150°C for 2 hours, under vacuum, 92.2 g of resin are obtained as a crystalline powder of white colour, having a higher melting point than 300°C.

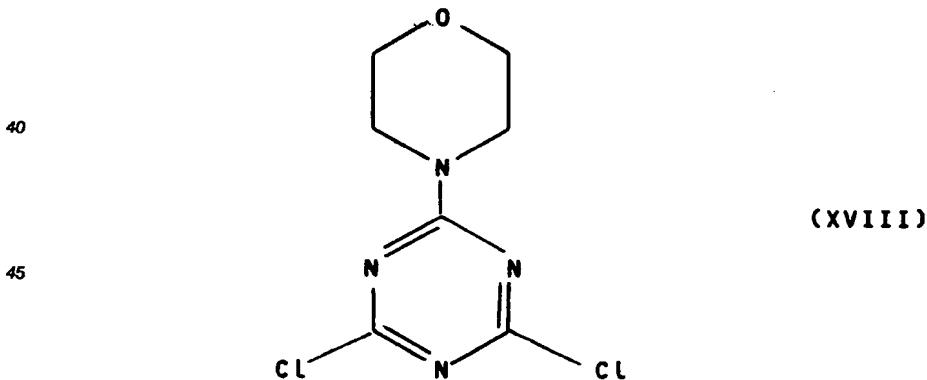
#### Example 2

30

184.5 g of cyanuric chloride and 1300 cm<sup>3</sup> of methylene chloride are charged to the same equipment of 3 litres of capacity as disclosed in Example 1.

Then, by proceeding as disclosed in Example 1, but using 87.2 g of morpholine, 230 g of intermediate (XVIII):

35



50

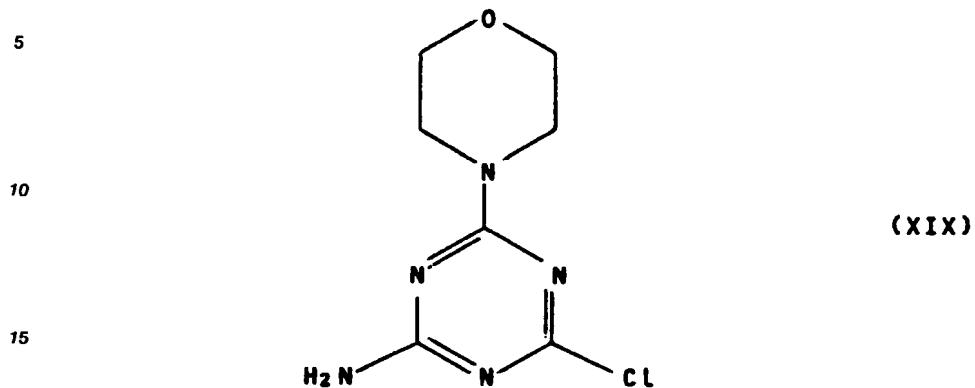
are obtained as a white crystalline powder with m.p. = 155–157°C and a chlorine content of 29.87% (theoretical value: 30.12%).

100 g of a solution at 30% by weight of ammonia

55 100 cm<sup>3</sup> of water and 70.5 g of intermediate (XVIII) are charged to a reactor of 0.5 litre of capacity, equipped as in Example 1.

The reaction mixture is heated up to 50°C and is kept 7 hours at this temperature; then, the reaction mixture is allowed to cool down to room temperature, the obtained product is filtered off and the filter cake is washed with water.

By drying the filter cake, 58 g of intermediate (XIX):

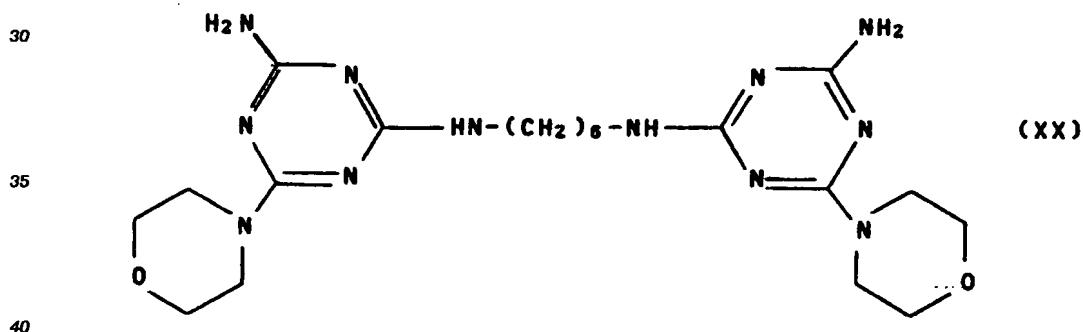


are obtained as a white crystalline powder with m.p. = 189–191 °C and a chlorine content of 16.28% (theoretical value: 16.47%).

20 400 cm<sup>3</sup> of ortho–dichlorobenzene, 53.9 g of intermediate (XIX) and 14.5 g of hexamethylenediamine are added to a reactor of 1 litre of capacity, fitted as the one disclosed hereinabove.

The resulting mixture is heated up to 100 °C, and is kept 2 hours at that temperature. Then, 10 g of sodium hydroxide are added and the resulting mixture is heated up to 140 °C. The reaction mixture is kept 25 16 hours at 140 °C, then is cooled down to room temperature and the resulting product is filtered off and the filter cake is washed with plentiful water.

After drying, 53.0 g of intermediate (XX):



are obtained as a white crystalline powder having m.p. = 267–269 °C.

The structure of compounds (XVIII), (XIX) and (XX) was confirmed by I.R. spectroscopic analysis.

45 400 cm<sup>3</sup> of water, 50.7 g of an aqueous solution at 37% by weight of formaldehyde, 0.5 g of sodium carbonate and, with stirring, 59.2 g of intermediate (XX) are charged to the same reactor of one litre of capacity.

The reaction mass is heated up to 65 °C, and is kept stirred at that temperature for 4 hours.

Then, 3.0 g of sulfuric acid are added, the reaction mass is heated up to boiling temperature, and is kept under refluxing conditions for 4 hours.

50 Then, 200 cm<sup>3</sup> of water are added, with the reaction temperature being allowed to decrease down to 50 °C, and the reaction mixture is subsequently neutralized by means of the addition of 2.6 g of sodium carbonate.

Then, by proceeding as disclosed in Example 1, 64.1 g of resin are obtained as a crystalline powder of white colour having a melting point higher than 300 °C.

Example 3

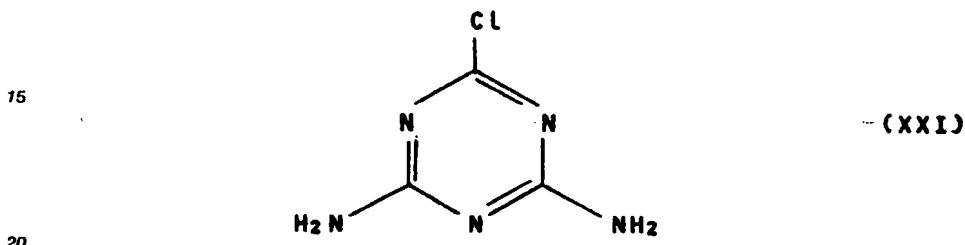
184.5 g of cyanuric chloride and 800 cm<sup>3</sup> of acetone are charged to a reactor of 3 litres of capacity, equipped with stirrer, thermometer, addition funnel, reflux condenser and heating bath.

5 With stirring, the reaction mixture is heated up to 40 °C in order to obtain a solution, then, with the temperature being kept at 40 °C, 284 g of an aqueous solution of ammonia at 30% by weight are added during a 1 hour and 30 minute time.

The reaction mixture is subsequently heated up to 45 °C and is kept 4 hours at this temperature.

After cooling, the resulting product is filtered off and is washed on the filter with water.

10 After oven drying at 50 – 60 °C under vacuum, 113 g of intermediate (XXI):



are obtained as a white, infusible, crystalline powder containing 24.2% of chlorine (theoretical chlorine content = 24.4%).

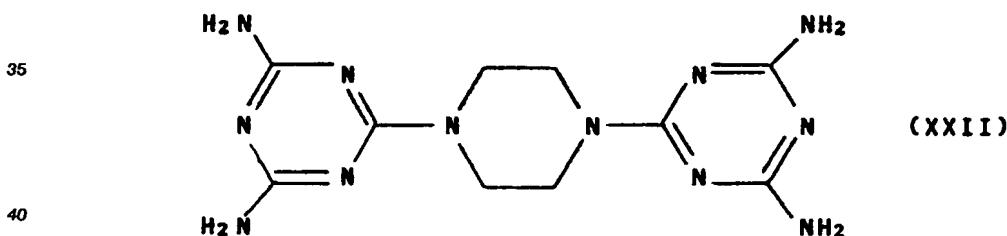
25 400 cm<sup>3</sup> of xylene, 58.2 g of intermediate (XXI) and 17.2 g of piperazine are charged to a reactor of 1 litre of capacity, fitted as the preceding one.

The reaction mass is heated up to 100 °C, and is kept 2 hours at this temperature.

Then, 16 g of sodium hydroxide in solid state are added and the resulting mixture is heated up to boiling temperature.

30 The reaction mixture is allowed to reflux for approximately 20 hours, then is cooled down to room temperature and is filtered.

The filter cake is washed with plentiful water and is dried. 54.2 g of intermediate (XXII):



are obtained as a white crystalline powder having a higher m.p. than 300 °C.

The structure of compounds (XXI) and (XXII) was confirmed by I.R. spectroscopic analysis.

45 400 cm<sup>3</sup> of water, 0.9 g of potassium carbonate, 72.9 g of an aqueous solution at 37% by weight of formaldehyde and, with stirring, 45.6 g of intermediate (XXII) are charged to the same reactor of one litre of capacity.

The reaction mass is heated up to 70 °C, and is kept stirred at that temperature for 6 hours.

50 Then, 3.0 g of sulfuric acid are added, the reaction mass is heated up to boiling temperature, and is kept under refluxing conditions for 6 hours.

Then, 150 cm<sup>3</sup> of water are added, with the reaction temperature being allowed to decrease down to 60 °C, and the reaction mixture is subsequently neutralized by means of the addition of 3.1 g of potassium carbonate.

55 The reaction mixture is kept at 60 °C for a further hour, than the resulting product is filtered off, and the filter cake is washed on the same filter with hot water.

After oven-drying the filter cake at 100 °C and submitting it to thermal treatment, 52.0 g of resin are obtained as a crystalline powder of white colour having a higher m.p. than 300 °C.

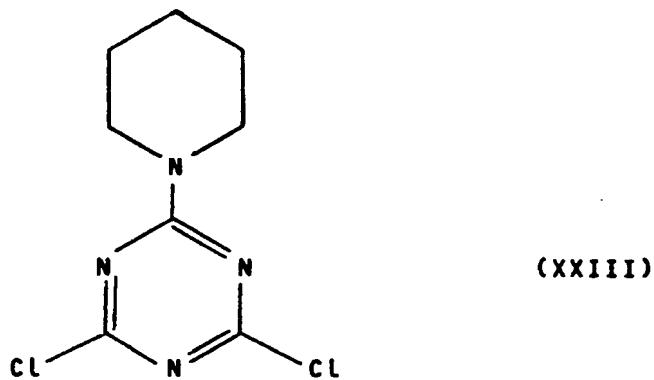
Example 4

184.5 g of cyanuric chloride and 700 cm<sup>3</sup> of water are charged to a reactor of 2 litres of capacity, fitted as in Example 1.

5 While cooling from the outside, 85 g of piperidine and 40 g of sodium hydroxide dissolved in 150 cm<sup>3</sup> of water are fed simultaneously during a 3 hour time, with the pH value of the mixture being kept comprised within the range of from 5 to 7, and the temperature being kept comprised within the range of from 0 to 3 °C.

10 The reaction mixture is kept at the temperature of 0–3 °C for a further 2 hours, then the resulting product is filtered off and is washed on the filter with water.

By drying the filter cake in an oven at 50 °C, under vacuum, 216.4 g of intermediate (XXIII):



are obtained as a white crystalline powder with m.p. = 73–75 °C, and a chlorine content of 30.26% (theoretical chlorine content: 30.47%).

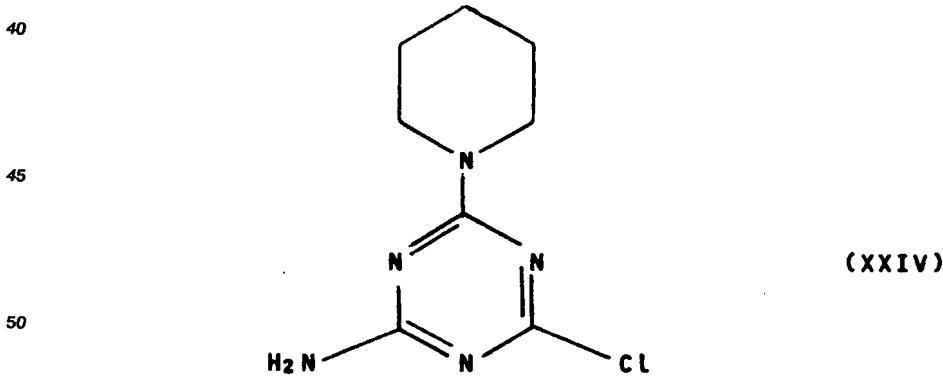
30 200 g of a solution of ammonia at 30% by weight and 500 cm<sup>3</sup> of water are charged to a reactor of 1 litre of capacity, fitted as in Example 1.

The reaction mixture is heated up to 40 °C and then, during a 30 minute time, 139.8 g of intermediate (XXIII) are added, with the reaction temperature being kept at 40 °C.

The reaction temperature is increased up to 45 °C and is kept at that value for approximately 6 hours.

35 At the end, the reaction is cooled down to room temperature and the resulting product is filtered off. The filter cake is washed with water and is dried.

123 g of intermediate (XXIV):



55 are obtained as a white crystalline powder having m.p. = 165–168 °C and containing 16.29% of chlorine (theoretical chlorine content: 16.63%).

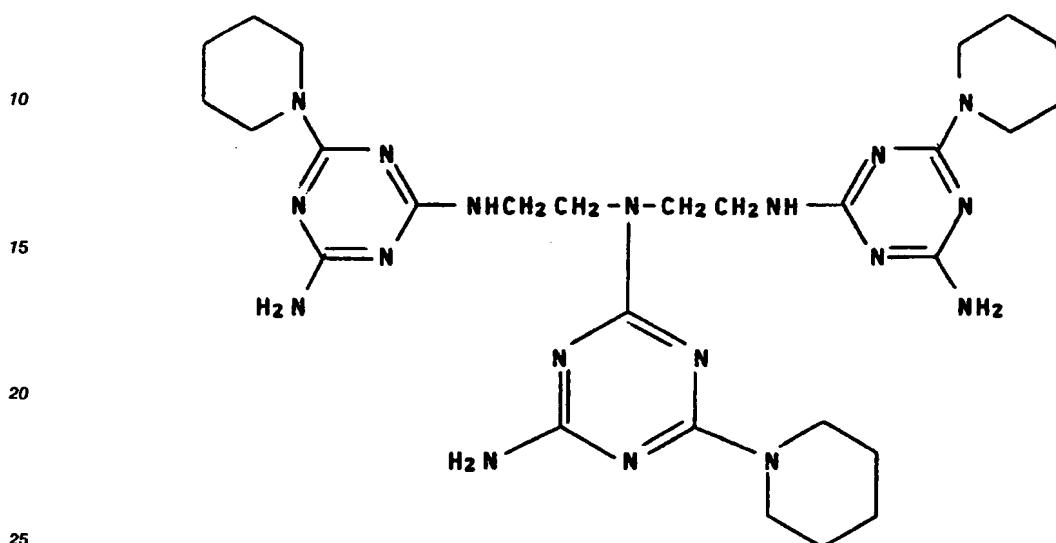
The structure of intermediates (XXIII) and (XXIV) was confirmed by NMR analysis.

600 cm<sup>3</sup> of xylene, 96.1 g of intermediate (XXIV) and 15.4 g of diethylene triamine are charged to the same reactor of 1 litre of capacity.

The reaction mixture is heated up to 100°C and is kept at that temperature for 2 hours. Then, 18 g of sodium hydroxide are added and the resulting mixture is heated up to boiling temperature.

The reaction mass is kept under refluxing conditions for 24 hours, then is cooled down to room temperature, the resulting product is filtered off and the filter cake is washed with water.

5 By oven - drying at 100°C, 93.1 g of intermediate (XXV):



(XXV)

30 are obtained as a white crystalline powder with m.p. = 259 - 262°C.

The structure of intermediate (XXV) is furthermore confirmed by I.R. spectroscopic analysis.

400 cm<sup>3</sup> of water, 64.9 g of a solution at 37% by weight of formaldehyde and, with stirring, 63.4 g of intermediate (XXV) are charged to the same reactor of one litre of capacity.

The reaction mixture is heated up to 60°C and is kept stirred at that temperature for 4 hours.

35 Then, 3.7 g of an aqueous solution at 37% by weight of hydrochloric acid are added, the reaction mixture is heated up to boiling temperature and is caused to reflux for 6 hours.

Then, 200 cm<sup>3</sup> of water are added, the reaction temperature is allowed to decrease down to 50°C and the mixture is neutralised by means of the addition of 1.5 g of sodium hydroxide.

40 The reaction mixture is kept for a further hour at 50°C, then the resulting product is filtered off, and the filter cake is washed on the same filter with hot water.

Then, by subsequently proceeding as disclosed in the above Examples, 71.2 g of resin are obtained as a crystalline powder of white colour having a melting point higher than 300°C.

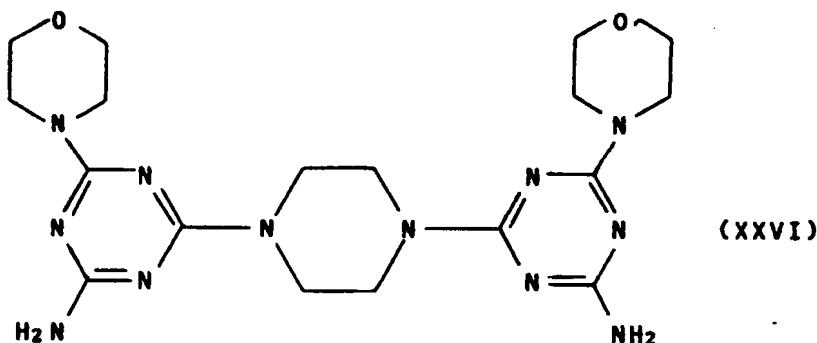
#### Example 5

45 600 cm<sup>3</sup> of xylene, 107.8 g of intermediate (XIX) and 21.5 g of piperazine are charged to a reactor of one litre of capacity equipped as Example 2.

Then, by proceeding as disclosed in Example 2, 106.1 g of intermediate (XXVI):

50

55



15 are obtained as a white crystalline powder having melting point = 280 - 285 °C.

The structure of intermediate (XXVI) was confirmed by IR spectroscopic analysis.

150 cm<sup>3</sup> of methanol, 100 cm<sup>3</sup> of water, 129.7 g of a solution at 37% by weight of formaldehyde and, with stirring, 66.6 g of intermediate (XXVI) and 31.5 g of 2,4,6-triamino-1,3,5-triazine (melamine) are charged to the same reactor of one litre of capacity.

20 The reaction mixture is heated up to 60 °C and is kept with stirring at that temperature for 4 hours.

Then, 2.9 g of phosphoric acid at 85% by weight diluted with 10 cm<sup>3</sup> of water are added, the reaction mixture is heated up to boiling temperature and is kept refluxing for approximately 10 hours.

Then 300 cm<sup>3</sup> of water are added, with the temperature being allowed to decrease down to 50 °C, and the mixture is neutralized by means of the addition of 4.3 g of potassium hydroxide.

25 The reaction mixture is kept at 50 °C for a further hour, then the resulting product is filtered off, and the filter cake is washed on the same filter with hot water.

Then, by proceeding according to the operating modalities as disclosed in the preceding Examples, 112.4 g of resin are obtained as a white crystalline powder, having a melting point higher than 300 °C.

30 Example 6

500 cm<sup>3</sup> of xylene, 86.2 g of intermediate (XIX) and 15.1 g of tetraethylenepentaamine are charged to a reactor of one litre of capacity, equipped as in the preceding Examples.

The reaction mixture is heated up to 80 °C and is kept at that temperature for two hours. Then, 16 g of 35 sodium hydroxide are added and the reaction temperature is increased up to 110 °C.

The reaction mass is kept at 100 °C for 18 hours, then is cooled down to room temperature, and the resulting product is filtered off, with the filter cake being washed with plentiful water on the same filter.

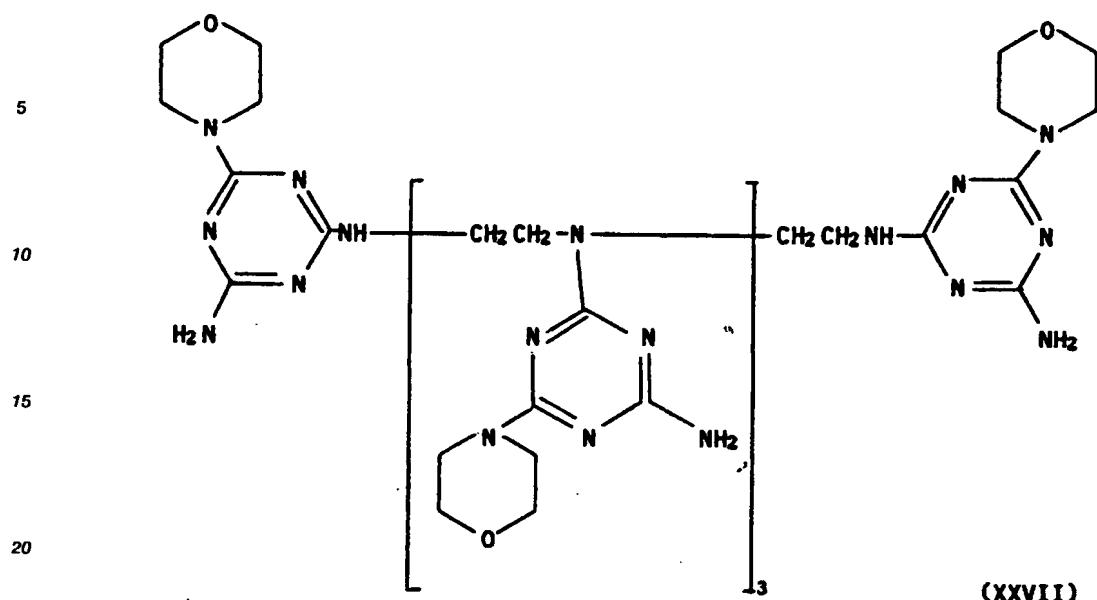
After drying the filter cake in an oven at 100 °C, 82.6 g of intermediate (XXVII):

40

45

50

55



are obtained as a white crystalline powder having melting point = 178–183 °C.

The structure of intermediate (XXVII) is also confirmed by IR spectroscopic analysis.

450 cm<sup>3</sup> of water, 0.5 g of sodium carbonate, 46.6 g of a solution at 37% by weight of formaldehyde and, with stirring, 54.2 g of intermediate (XXVII) are charged to the same reaction equipment of 1 litre of capacity.

By operating analogously to as disclosed in the preceding Examples, the reaction mixture is heated 4 hours at 60 °C, is acidified with 7.9 g of an aqueous solution at 48% by weight of hydrobromic acid and is kept 8 hours under refluxing conditions.

The reaction mixture is then diluted with 200 cm<sup>3</sup> of water, is cooled down to 50 °C, and is neutralized with 1.5 g of sodium hydroxide.

After filtering off the product, drying the filter cake and carrying out the thermal conditioning of the compound, 67.8 g of resin are obtained as a white crystalline powder having a higher melting point than 300 °C.

Example 7

40 450 cm<sup>3</sup> of water, 91.6 g of intermediate (XVI), and, with stirring, 21.9 g of tris (2-aminoethyl) amine are charged to a reactor of 1 litre of capacity, equipped as disclosed in the preceding Examples. The reaction mixture is heated up to 80 °C and is kept at that temperature for 3 hours.

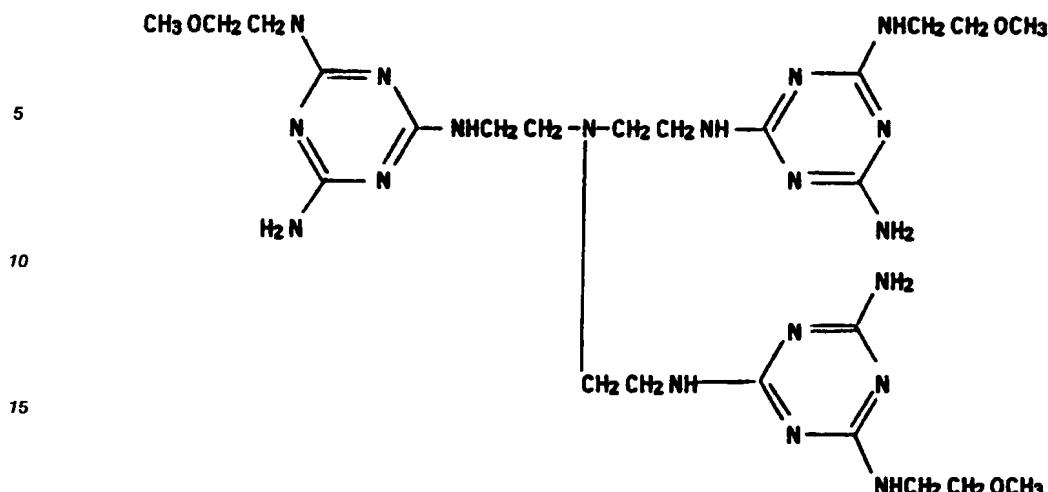
Then 18 g of sodium hydroxide dissolved in 30 cm<sup>3</sup> of water are added, and the reaction mixture is heated up to boiling temperature.

45 The reaction mixture is caused to reflux for 16 hours, then is cooled down to 10 °C, and the resulting product is filtered off, with the filter cake being washed on the same filter with cold water.

By drying the filter cake in an oven at 100 °C, 85.4 g of intermediate (XXVIII):

50

55



are obtained as a white crystalline powder,  
having melting point = 190–195 °C.

The structure of intermediate (XXVIII) was also confirmed by NMR analysis.

25 300 cm<sup>3</sup> of water, 0.7 g of sodium carbonate, and, with stirring, 24.0 g of paraformaldehyde and 64.7 g of intermediate (XXVIII) are charged to the same reactor of 1 litre of capacity.

The reaction mixture is heated up to 45 °C and is kept at that temperature for 6 hours.

Then, 3.0 g of sulfuric acid at 96% are added, the resulting mixture is heated up to boiling temperature and is caused to reflux for approximately 8 hours.

30 250 cm<sup>3</sup> of water are added, the resulting mixture is cooled down to 45 °C and is neutralized by means of the addition of 2.4 g of sodium carbonate.

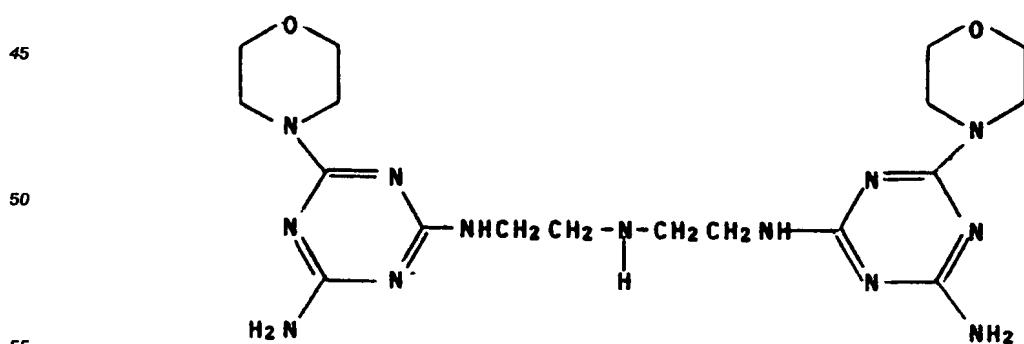
Then, by proceeding as disclosed in the preceding Examples, 72.9 g of resin are obtained as a white crystalline powder having a higher m. p. than 300 °C.

35 **Example 8**

400 cm<sup>3</sup> of water, 86.2 g of intermediate (XIX) and 20.6 g of diethylenetriamine are charged to the same equipment of 1 litre of capacity, as of the preceding Example.

The reaction mass is heated at 80 °C for two hours, then 16 g of sodium hydroxide dissolved in 30 cm<sup>3</sup> 40 of water are added, and the reaction mixture is heated up to boiling temperature.

The reaction mixture is caused to reflux for approximately 14 hours, then, by proceeding as disclosed in the preceding Example, 86.2 g of intermediate (XXIX):



are obtained as a white crystalline powder,  
having melting point = 198–201 °C.

The structure of intermediate (XXIX) was further confirmed by IR spectroscopic analysis.

350 cm<sup>3</sup> of water, 77.9 g of a solution at 37% by weight of formaldehyde and, with stirring, 73.8 g of 5 intermediate (XXIX) are charged to the same reactor of 1 litre of capacity.

The reaction mixture is heated up to 50 °C and is kept at that temperature for 3 hours.

The resulting mixture is acidified with 4.1 g of hydrochloric acid at 37% by weight, then is heated up to boiling temperature and is caused to reflux for 4 hours.

Then 250 cm<sup>3</sup> of water are added, the resulting mixture is allowed to cool down to 60 °C, and is 10 neutralized by means of the addition of 2.2 g of potassium carbonate.

By proceeding as in the preceding Examples, 85.8 g of resin are obtained as a crystalline powder of white colour having a higher melting point than 300 °C.

#### Example 9

15

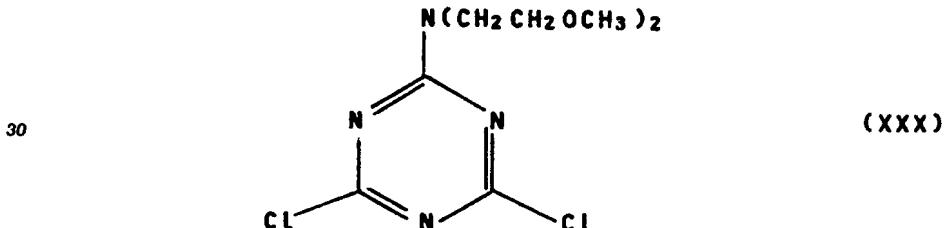
184.5 g of cyanuric chloride and 700 cm<sup>3</sup> of water are charged to a reactor of 2 litres of capacity, equipped as in Example 4.

With external cooling, 133 g of bis (2-methoxyethyl) amine and 40 g of sodium hydroxide dissolved in 150 cm<sup>3</sup> of water are added simultaneously during a 3 hours time, with the pH value of the reaction mixture 20 being kept comprised within the range of from 5 to 7 and the reaction temperature within the range of from 0 to 3 °C.

The reaction mixture is kept at the temperature of 0–3 °C for a further two hours, then the resulting product is filtered off and the filter cake is washed on the filter with cold water.

By oven drying the filter cake at 50 °C under vacuum, 254.3 g of intermediate (XXX):

25



are obtained as a white crystalline powder having melting point = 63 – 65 °C, and containing 25.06% of chlorine (theoretical chlorine content: 25.27%).

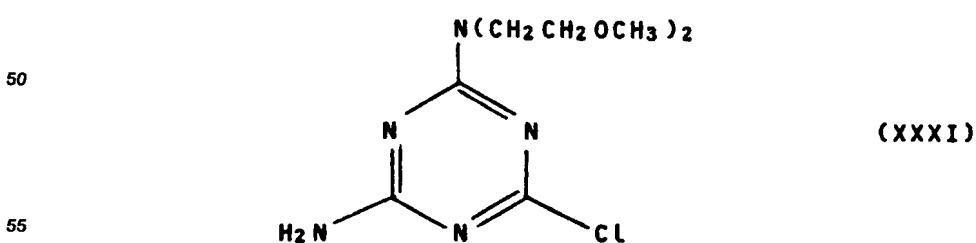
200 g of a solution of ammonia at 30% by weight and 500 cm<sup>3</sup> of water are charged to a reactor of one 40 litre of capacity, equipped as in the preceding Examples.

The reaction mixture is heated up to 40 °C and then 168.6 g of intermediate (XXX) are added during a 30 minute time, with the reaction temperature being kept at 40 °C.

The reaction temperature is increased up to 45 °C and is kept at that value for approximately 6 hours.

At the end, the reaction mixture is cooled down to the temperature of 10 °C, the resulting product is 45 filtered off, and the filter cake is washed on the same filter with cold water.

By oven-drying the filter cake, 139.4 g of intermediate (XXXI):



are obtained as a white crystalline powder

having melting point = 87 - 88°C and containing 13.39% of chlorine (theoretical chlorine content: 13.57%).

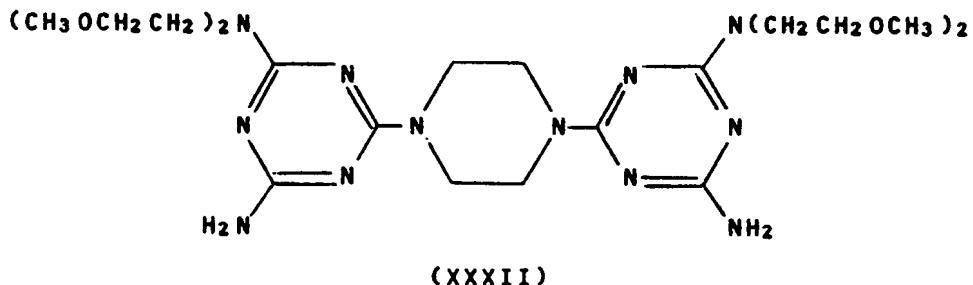
The structure of intermediates (XXX) and (XXXI) was further confirmed by NMR analysis.

5 600 cm<sup>3</sup> of xylene, 130.8 g of intermediate (XXXI) and 21.5 g of piperazine are charged to the same reactor of one litre of capacity.

The reaction mixture is heated up to 100°C and is kept at that temperature for 2 hours. Then, 20 g of sodium hydroxide are added and the resulting mixture is heated up to boiling temperature.

10 The reaction mixture is caused to reflux for 24 hours, then is cooled down to room temperature, and the resulting product is filtered off, with the filter cake being washed with plentiful water.

By oven-drying at 100°C, 126.1 g of intermediate (XXXII):



25 are obtained as a white crystalline powder having melting point = 168 - 170°C.

The structure of intermediate (XXXII) is furthermore confirmed by IR spectroscopic analysis.

30 350 cm<sup>3</sup> of water, 0.5 g of sodium carbonate, 32.5 g of a solution at 37% by weight of formaldehyde and, with stirring, 53.6 g of intermediate (XXXII) are charged to the same reactor of one litre of capacity.

The reaction mass is heated up to 65°C and is kept 5 hours at that temperature, with stirring.

35 30 Then, 3.0 g of sulfuric acid is added, the reaction mixture is heated up to boiling temperature, and is caused to reflux of 5 hours.

250 cm<sup>3</sup> of water are added, with the reaction temperature being allowed to decrease down to 50°C and the resulting mixture is neutralized by means of the addition of 2.6 g of sodium carbonate.

35 The reaction mixture is kept at 50°C for a further hour, then the resulting product is filtered off, and the filter cake is washed on the same filter with hot water.

Then, by subsequently proceeding as disclosed in the preceding Examples, 55.1 g of resin are obtained as a white crystalline powder having a melting temperature higher than 300°C.

#### Examples 10 - 22

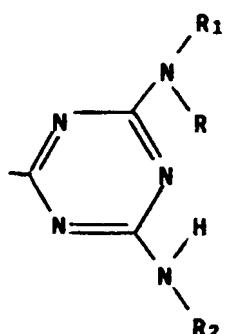
40

By operating under analogous conditions to as disclosed in Examples from 1 to 9, the resins of melaminic derivatives of general formula (I), either containing, or not containing, polyaminic compounds, as reported in Table 2 and having higher melting points than 300°C are prepared by polymerization with formaldehyde. In such structures, the radical R<sub>3</sub>, when present, is replaced by the triazinic ring of formula:

45

50

55



5  
10  
15  
20  
25  
30  
35  
40  
45  
50

TABLE 2

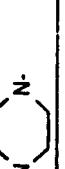
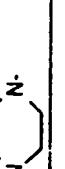
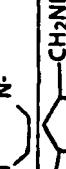
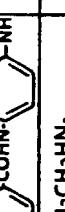
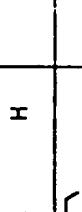
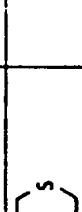
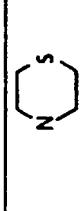
EXAMPLE N°	Derivative of general formula (I)			Polyaminic derivative	R <sub>4</sub> - CHO	Molar ratio polyamines aldehydes
	R	N	R <sub>1</sub>			
10		H		$-Z - \left[ \begin{array}{c} N \\   \\ Z_2 \end{array} \right]_a \left[ \begin{array}{c} N \\   \\ Z_1 \end{array} \right]_b -$ $-HNC_2H_4-N-C_2H_4NH-$	—	—
11	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	H	H		—	—
12	H	H	H	$-HNCH_2CH_2NH-$	—	1:8
13		H			—	—
14	(CH <sub>2</sub> ) <sub>2</sub> OCH=CH <sub>2</sub>	H	H		—	—
15	H	H	H	$-HNC_2H_4-N-C_2H_4NH-$	—	1:10
16	CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	H	H		Ethylene- urea 40	—
17		H		$-HNCH_2-\text{cyclohexyl}-CH_2NH-$	—	1:4

TABLE 2 (continuation)

EXAMPLE N°	Derivative of general formula (I)			Polyaminic derivative designation by weight	R <sub>4</sub> · CHO	Molar ratio polyamines aldehydes
	R	—N—R <sub>1</sub>	R <sub>2</sub>			
18	(CH <sub>2</sub> ) <sub>3</sub> OCH <sub>3</sub>	H	H		—	—
19		H	H		—	—
20	(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> OH	H	H		—	—
21	CH <sub>2</sub> · CH = CH <sub>2</sub>	H	H		—	—
22	CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	H	H		melamine 41	—

## Example 23

55

75 g of isotactic polypropylene flakes, having a Melt Flow Index equal to 12 and containing 96% by weight of insolubles in n-heptane; 5.4 g of the product of Example 3; 21.6 g of ammonium polyphosphate (Exolit 422 ex Hoechst); 0.67 g of dilauryl thiopropionate and 0.33 g of pentaerythritol tetra [3-(3,5-di-tert

– butyl – 4 – hydroxyphenyl) propionate] are blended and moulded on a MOORE platen press, by operating for 7 minutes at a pressure of 40 kg/cm<sup>2</sup>.

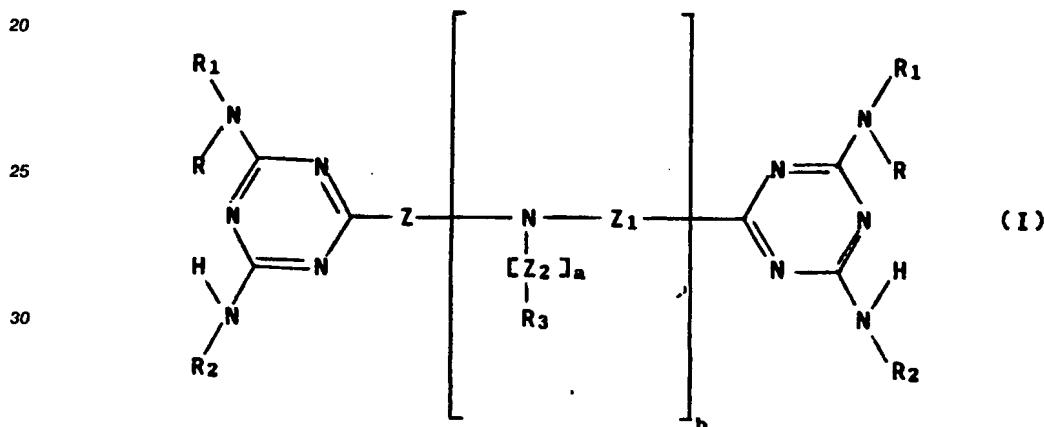
Specimens are obtained as small slabs of approximately 3 mm of thickness, and on them the level of self – extinguishment is determined by measuring the oxygen index (L.O.I. according to ASTM D – 2863/77) 5 on a STANTON REDCROFT instrument, and applying the "Vertical Burning Test", which makes it possible the material to be classified at the three levels 94 V – 0,94 V – 1 and 94 V – 2 according to UL 94 standards (published by "Underwriters Laboratories" – USA).

The following results are obtained:

L.O.I. = 36.8  
10 UL 92 = Class V – 0.

### Claims

1. Aminoplastic resins obtained by means of the polymerisation of a mixture comprising:  
15 (1) from 0 to 50 parts by weight of one or more polyaminic derivatives;  
(2) from 50 to 100 parts by weight of one or more derivatives of 2,4,6 – triamino – 1,3,5 – triazine having the general formula (I):

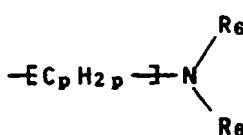
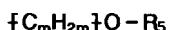


wherein the aldehyde having the general formula (II) is present in an amount of up to 20% by mol, and

wherein:

the radicals from R to  $R_2$ , which may be the same, or different from each other, and may have different meanings on each triazinic ring, are:

$H$ ;  $C_1 - C_{18}$  alkyl;  $C_2 - C_8$  alkenyl;  $C_6 - C_{16}$  cycloalkyl or alkylcycloalkyl, possibly substituted with a hydroxy or  $C_1 - C_4$  hydroxyalkyl function;



wherein:

$m$  = an integer comprised within the range of from 2 to 8;

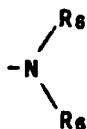
p = an integer comprised within the range of from 2 to 6;

R<sub>6</sub> = H; C<sub>1</sub> - C<sub>8</sub> alkyl; C<sub>2</sub> - C<sub>6</sub> alkenyl;  $-[-C_qH_{2q}-]O-R_7$  wherein q is an integer comprised within the range of from 1 to 4 and R<sub>7</sub> is H or C<sub>1</sub> - C<sub>4</sub> alkyl; C<sub>6</sub> - C<sub>12</sub> cycloalkyl or alkylcycloalkyl;

5 the radicals R<sub>6</sub>, which may be the same, or different from each other, are:

H, C<sub>1</sub> - C<sub>8</sub> alkyl; C<sub>2</sub> - C<sub>6</sub> alkenyl; C<sub>6</sub> - C<sub>12</sub> cycloalkyl or alkylcycloalkyl; C<sub>1</sub> - C<sub>4</sub> hydroxyalkyl; or the moiety:

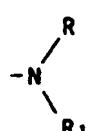
10



15

is replaced by a heterocyclic radical linked to the alkyl chain through the nitrogen atom, and possibly containing another heteroatom;  
or in the general formula (I) the moiety:

20



25

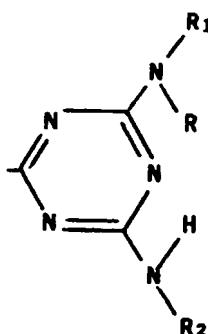
is replaced by a heterocyclic radical linked to the triazinic ring through the nitrogen atom, and possibly containing another heteroatom;

a is 0 (zero) or 1;

30 b is 0 (zero) or an integer comprised within the range of from 1 to 5;

R<sub>3</sub> is hydrogen or:

35



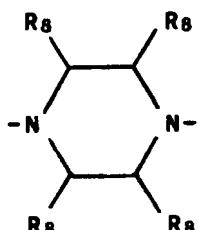
40

45

and its meaning may vary within each repeating unit; when b is 0 (zero), Z is a divalent radical falling within the scope of one of the following formulas:

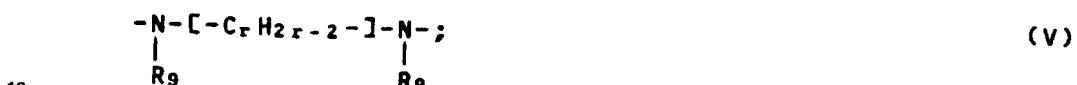
50

55

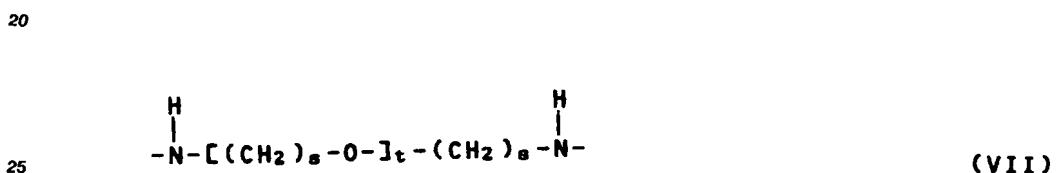
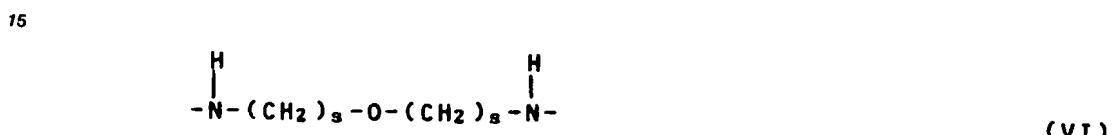


(III)

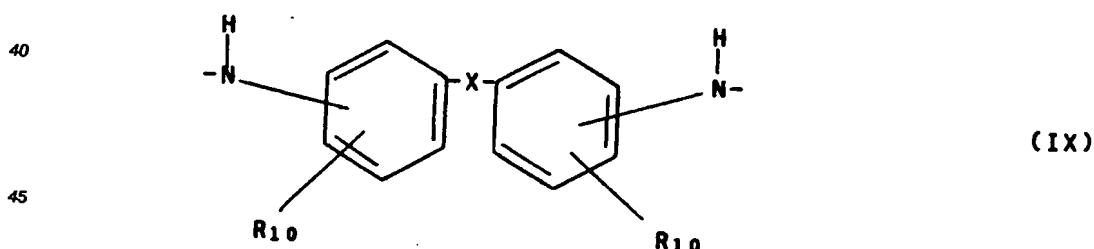
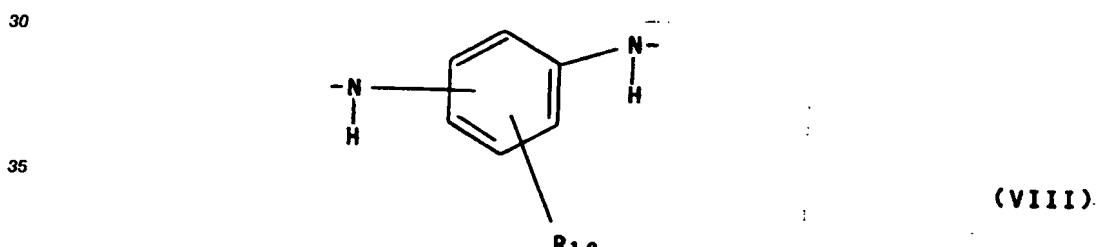
wherein the radicals  $R_8$ , which may be the same or different from each other, are hydrogen or  $C_1 - C_4$  alkyl;



wherein  $r$  is an integer comprised within the range of from 2 to 14;  $R_9$  is hydrogen;  $C_1 - C_4$  alkyl;  $C_2 - C_6$  alkenyl;  $C_1 - C_4$  hydroxyalkyl;

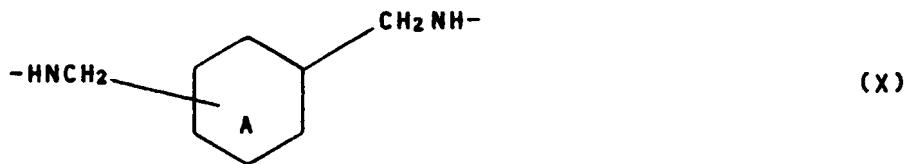


wherein  $s$  is an integer comprised within the range of from 2 to 5 and  $t$  is an integer comprised within the range of from 1 to 3;

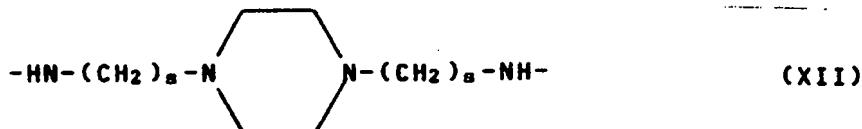


wherein:

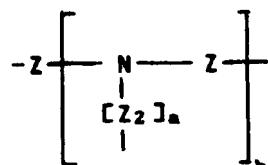
50  $X$  is a direct C-C bond; O; S; S-S; SO;  $SO_2$ ; NH;  $NHSO_2$ ;  $NHCO$ ;  $N=N$ ;  $CH_2$ ;  
 $R_{10}$  is hydrogen; hydroxy;  $C_1 - C_4$  alkyl;  $C_1 - C_4$  alkoxy;



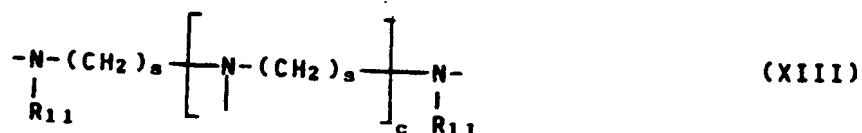
10 wherein A may be a saturated or unsaturated ring;



25 wherein s has the above defined meaning;  
when, on the contrary, b is an integer comprised within the range of from 1 to 5, the moiety:

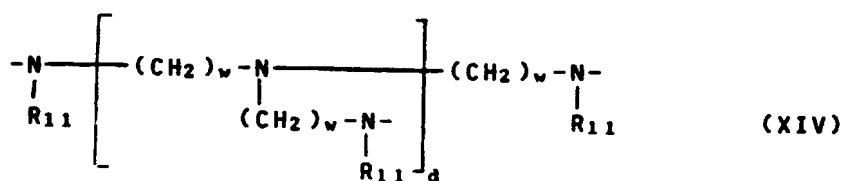


35 is a multivalent moiety falling within the scope of one of the following formulas:



wherein:

45 R<sub>11</sub> is hydrogen or C<sub>1</sub> - C<sub>4</sub> alkyl;  
c is an integer comprised within the range of from 1 to 5;  
the indexes s, which may be the same, or different from each other, have the same meaning as defined hereinabove;

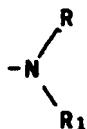


wherein:

R<sub>1</sub> has the meaning as defined hereinabove;  
 w is an integer comprised within the range of from 2 to 4;  
 d is either 1 or 2.  
 R<sub>4</sub> is C<sub>1</sub> - C<sub>8</sub> alkyl; C<sub>2</sub> - C<sub>6</sub> alkenyl; C<sub>6</sub> - C<sub>12</sub> cycloalkyl; C<sub>6</sub> - C<sub>12</sub> aryl, possibly substituted with one or more C<sub>1</sub> - C<sub>4</sub> alkyl radicals; C<sub>7</sub> - C<sub>16</sub> aralkyl; C<sub>8</sub> - C<sub>12</sub> aralkenyl.

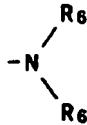
5 2. Aminoplastic resins according to claim 1, in which the polyaminic derivative is selected from compounds containing the 1,3,5-triazine ring, or at least one >C=O and/or >C=S moiety.

10 3. Aminoplastic resins according to claims 1 or 2, in which the moiety:



in general formula (I) is replaced by heterocyclic radicals selected from:  
 20 aziridine; pyrrolidine; piperidine; morpholine; thiomorpholine; piperazine; 4-methylpiperazine; 4-ethylpiperazine; 2-methylpiperazine; 2,5-dimethylpiperazine; 2,3,5,6-tetramethylpiperazine; 2,2,5,5-tetramethylpiperazine; 2-ethylpiperazine; 2,5-diethylpiperazine.

25 4. Aminoplastic resins according to claim 1, 2 or 3, in which the moiety:



is replaced by a heterocyclic radical selected from: aziridine; pyrrolidine; piperidine; morpholine; thiomorpholine; piperazine; 4-methylpiperazine; 4-ethylpiperazine.

35 5. Aminoplastic resins according to any of the preceding claims, in which the polyaminic derivative is selected from:  
 urea; ethyleneurea; propyleneurea; thiourea; ethylenethiourea; melamine; acetoguanamine; propionoguanamine; butyroguanamine; isobutyroguanamine; caprinoguanamine; succinoguanamine; benzoguanamine; meta-methylbenzoguanamine; benzylguanamine; hydantoin; piperazine-2,5-dione; barbituric acid.

40 6. Aminoplastic resins according to any of the preceding claims, in which R<sub>4</sub> radical is selected from:  
 methyl; ethyl; n-propyl; isopropyl; n-butyl; isobutyl; tert-butyl; n-pentyl; isopentyl; n-hexyl; n-heptyl; isoheptyl; n-octyl; ethenyl; propenyl; isobut enyl; sec-but enyl; n-pentenyl; cyclohexyl; phenyl; 2-methylphenyl; 3-methylphenyl; 4-methylphenyl; 4-isopropylphenyl; 2,4,6-trimethylphenyl; 1-phenylethyl; 2-phenylethyl; 2-phenylethenyl.

45 7. Process for preparing the aminoplastic resins according to any of the preceding claims, comprising:  
 (a) reacting the derivative of general formula (I), either mixed with the polyaminic derivative, or not mixed with it, with formaldehyde or a mixture of formaldehyde containing up to 20% by mol of an aldehyde of general formula (II);  
 (b) acidifying the resulting reaction product down to a pH value comprised within the range of from 1 to 5.

55 8. Process according to claim 7, in which the reaction (a) is carried out with a molar ratio of the derivative of general formula (I), or its mixture with the polyaminic derivative, to formaldehyde, or its mixture with the aldehyde of general formula (II), comprised within the range of from 1:1 to 1:12.

9. Process according to claim 7 or 8, in which the reaction (a) is carried out at a temperature comprised within the range of from 20 °C to the boiling point of the solvent used, and the reaction (b) is carried out at a temperature comprised within the range of from 40 °C up to the boiling point of the solvent.

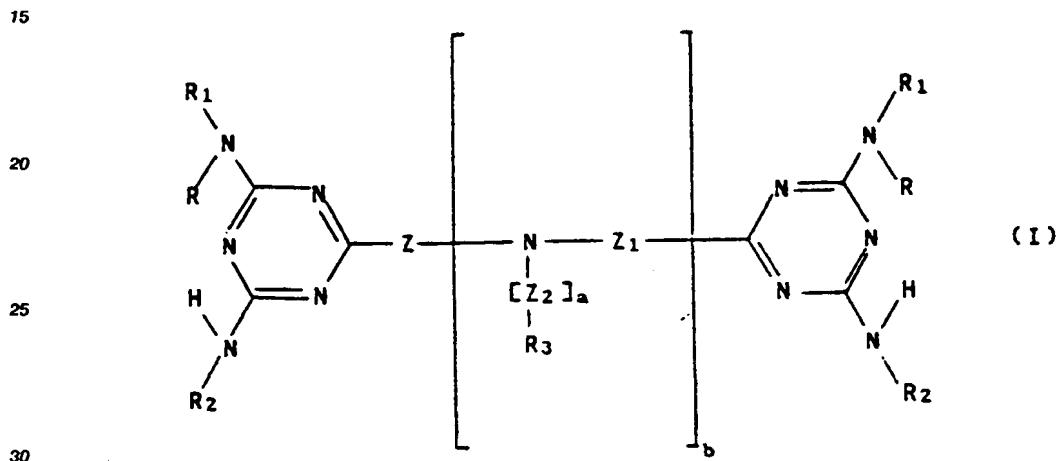
5 10. Process according to claim 7, 8 or 9, in which the reactions of (a) and (b) stages are carried out in one single step at a temperature higher than 40 °C.

## Amended claims in accordance with Rule 86(2) EPC.

10 1. Aminoplastic resins obtained by means of the polymerisation of a mixture comprising:

(1) from 0 to 50 parts by weight of one or more polyaminic derivatives;

(2) from 50 to 100 parts by weight of one or more derivatives of 2,4,6-triamino-1,3,5-triazine having the general formula (I):



with formaldehyde or a mixture of formaldehyde and an aldehyde having the general formula (II):

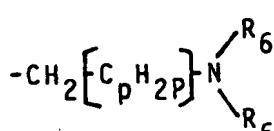


wherein the aldehyde having the general formula (II) is present in an amount of up to 20% by mol, and

wherein:

40 the radicals from R to R<sub>2</sub>, which may be the same, or different from each other, and may have different meanings on each triazinic ring, are:

45 H; C<sub>1</sub> - C<sub>18</sub> alkyl; C<sub>2</sub> - C<sub>6</sub> alkenyl; C<sub>6</sub> - C<sub>16</sub> cycloalkyl or alkylcycloalkyl, possibly substituted with a hydroxy or C<sub>1</sub> - C<sub>4</sub> hydroxyalkyl function;



wherein:

m = an integer comprised within the range of from 1 to 7;

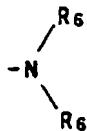
p = an integer comprised within the range of from 1 to 5;

R<sub>5</sub> = H; C<sub>1</sub> - C<sub>8</sub> alkyl; C<sub>2</sub> - C<sub>6</sub> alkenyl;  $-[-C_qH_{2q}-]O-R_7$  wherein q is an integer comprised within the range of from 1 to 4 and R<sub>7</sub> is H or C<sub>1</sub> - C<sub>4</sub> alkyl; C<sub>6</sub> - C<sub>12</sub> cycloalkyl or alkylcycloalkyl;

the radicals  $R_6$ , which may be the same, or different from each other, are:

H,  $C_1 - C_8$  alkyl;  $C_2 - C_6$  alkenyl;  $C_6 - C_{12}$  cycloalkyl or alkylcycloalkyl;  $C_1 - C_4$  hydroxyalkyl; or the moiety:

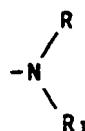
5



10

is replaced by a heterocyclic radical linked to the alkyl chain through the nitrogen atom, and possibly containing another heteroatom;  
or in the general formula (I) the moiety:

15



20

is replaced by a heterocyclic radical linked to the triazinic ring through the nitrogen atom, and possibly containing another heteroatom;

25

30

35

40

45

50

55



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 92 20 3471

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
Y	US-A-2 524 727 (J. R. DUDLEY) * claims 1-18; figures 1,2; examples * ---	1-6	C08G12/30
Y	EP-A-0 448 774 (MINISTERO DELL'UNIVERSITA'E DELLA RICERCA SCIENTIFICA E TECHNOLOGICA) * claims; examples *	1-6	
A	US-A-2 339 622 (G. F'ALELIO) * claims *	1	
A	US-A-2 544 071 (J. DUDLEY) -----		
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			C08G C07D
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	18 FEBRUARY 1993	KLER E.K.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			